A Microfluidic Device for the Investigation of Rapid Gold Nanoparticle Formation in

Continuous Turbulent Flow

You may also be interested in:

Numerical study of nanoparticle formation in a free turbulent jet
A K Gilfanov, W Koch, S K Zaripov et al.

Nanocrystallization Mechanism of Organic Compounds in the Reprecipitation Method by Stopped-Flow
Analysis
Daniel Oliveira, Koichi Baba, Junichi Mori et al.

Nanoparticle formation in the expansion process of a laser ablated plume
T Takiya, I Umezu, M Yaga et al.

Nanoparticle Formation of Pentacene by Laser Irradiation in Ethanol Solution
Shinji Kita, Sadahiro Masuo, Shinjiro Machida et al.

Thermal induced structural transformation of bimetallic AuPd nanoparticles
A Bruma and Z Y Li

Synthesis and characteristics of Ag/Pt bimetallic nanocomposites by arc-discharge solution plasma
processing
Panuphong Pootawang, Nagahiro Saito, Osamu Takai et al.

Analysis of the inter- and extracellular formation of platinum nanoparticles by Fusariumoxysporum
f. sp. Lycopersici using response surface methodology
T L Riddin, M Gericke and C G Whiteley

Nanoparticle formation in Au thin films by electron-beam-induced dewetting
Yasuhiko Kojima and Takahisa Kato

A Microfluidic Device for the Investigation of Rapid Gold Nanoparticle Formation in Continuous Turbulent Flow

G Hofmann[1], G Tofighi[1], G Rinke[2], S Baier[1], A Ewinger[2], A Urban[2], A Wenka[2], S Heideker[2], A Jahn[3], R Dittmeyer[2], J-D Grunwaldt[1,4]

[1] Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe, Germany

[2] Karlsruhe Institute of Technology, Institute for Micro Process Engineering (IMVT), Karlsruhe, Germany

[3] TU Dresden, Institute of Semiconductors and Microsystems, Dresden, Germany

[4] Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology (IKFT), Karlsruhe, Germany

E-mail: grunwaldt@kit.edu

Abstract. A new setup with an integrated microfluidic chip with small dead time, high time resolution and compatibility with *in situ* X-ray absorption (XAS) measurements is presented. It can also be combined with a free liquid jet. By using the microfluidic chip the short reaction times from 2 to 20 milliseconds can be observed, beyond that an external cyclone mixer for extended observation times was applied. The reduction of gold ions with tetrakis(hydroxymethyl)phosphonium (THPC) has been investigated in the microfluidic setup to monitor this reaction yielding small gold nanoparticles, requiring preferentially a free liquid jet.

1. Introduction

Gold nanoparticles (AuNPs) have found various applications in a broad range of scientific fields like medicine and catalysis. Their versatility and suitability in many different applications is due to the fact that gold particles of different size and shape can be prepared [1]. The need for defined AuNPs calls for a better control of the process, knowledge of the reaction mechanisms and kinetics, especially in the early phase of nucleation [2, 3]. For this purpose *in situ* studies are inevitable and microfluidic devices offer the opportunity to provide rapid and thorough mixing [4-6] and to shine X-rays through them. The formation of AuNPs was successfully studied using X-ray absorption spectroscopy (XAS), small angle X-ray scattering (SAXS), and UV-VIS for citrate and BH_4 based synthesis routes [7-9]. Notably, a fast gold reduction was observed within the first 200 ms. However, observations of the first 100 ms of reaction were not possible due to the experimental setup or acquisition time of the spectroscopic method used in the stopped flow apparatus, respectively. Therefore, it is required to aim at a fast data acquisition in case of stopped flow or measurements in continuous flow to enhance time resolution at the very early stage of the reaction. This would allow covering the initial growth kinetics or correlating time and measurement position to enhance resolution.

In this work, a first setup with very small dead time and high time resolution is presented. Next, the reaction process can be evaluated by XAS measurements with an option to also use SAXS as complementary technique at a later stage. The reduction of $HAuCl_4$ with tetrakis(hydroxymethyl)phospho-

nium chloride (THPC) was chosen [10] to understand this rapid reaction yielding small Au nano-particles suitable for catalysis. Note that up to now mainly the late growth phase of AuNPs from THPC was studied yet from 10 to 700 minutes [1,11,12].

2. Experimental Principle and Setup

A high time resolution of the reaction process requires either a very fast acquisition after start of the reaction, which needs a high X-ray flux in order to achieve a good signal to noise ratio, or a method to correlate the result of a "slow" measurement to a specific reaction time. Here, a continous flow microreactor setup was used and the location in the channel or its length corresponds to a certain reaction time [13]. The basic setup is depicted in Figure 1. Both good mixing is and a stable and predictable residence time are important. For this purpose, a micromixer based on a previous design [4] was used and a high flow rate was applied (Reynolds number above 2300 in the channel) to establish a plug flow with a flat flow velocity profile; the rapid mixing ensures that the reaction kinetics are not determined by the diffusion. In this way, a measurement of the reaction mixture at a given position in the channel corresponds to a specific time of the reaction after mixing; on the other hand the fluid can be monitored at the outlet. The experiments were conducted at beamline P06 (PETRA III) using a fluorescence detector for measuring the fluorescence XAS data [13].
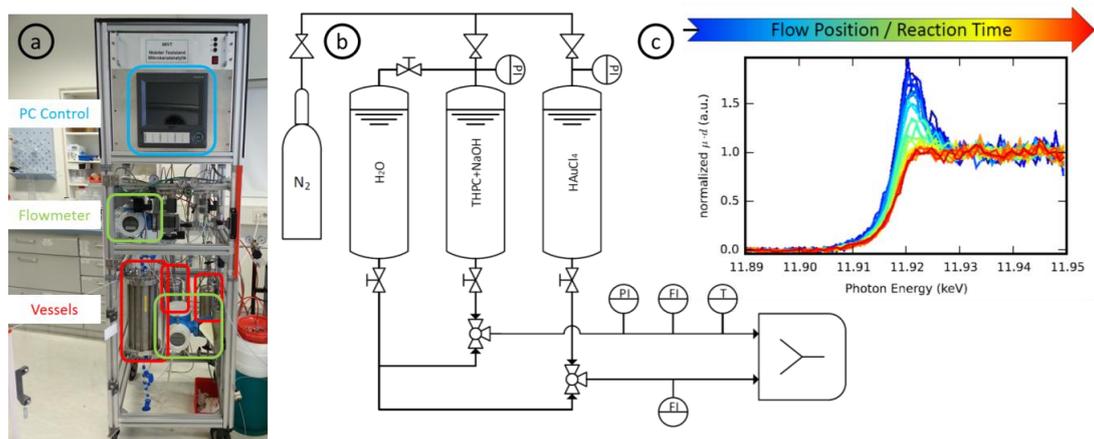
Figure 1. a) Photograph, b) schematic drawing of the fluid delivery rack and c) principle for monitoring gold reduction. The rack is grouped into three parts: Vessels, flowmeters, and PC control. Fluids are stored in vessels pressurized by nitrogen gas and are delivered to a microfluidic mixer to be rapidly and thoroughly mixed. The flow to the microfluidic mixer can be adjusted for each branch. The continuous product flow is then measured at several positions, which are mapped to reaction time (not shown). Symbols: PI= pressure indicator, FI= flow indicator, and T= temperature detection.

Sufficiently high and pulsation-free flow rates were provided by a home-built fluidic rack (Fig. 1a). The vessels and all fluidic parts are designed to be pressure resistant up to 15 bars, which is required to achieve a suitably high flow rate. In addition, the vessel, flowmeter, and the branch for the gold pre-cursor solution is kept fully corrosion resistant and chemically inert. The microfluidic mixer as the next key part of the setup was optimized and designed based on computational fluid dynamics (CFD) simulations to obtain a perfect mixing in a short time with little residence time. In Figure 2 a) one simulation is shown for the resulting triple cyclone mixer, which is based on developments at IMVT-KIT [6]. In order to measure the liquid as soon as possible after mixing, the mixer was built into a Si-based microfluidic chip, which features observation lines directly attached to the mixer outlet. A schematic drawing of the microfluidic chip is shown in Figure 2 b). The chip to monitor liquid phase reactions was fabricated in collaboration with GeSiM GmbH and IHM TUD. The chip with a thickness of 1500 μm was obtained by Si fusion bonding of two 750 μm wafers with a diameter of 4 inch. This chip contained the integrated micro fluidic mixer and a 300×300 μm fluidic channel (called "observation line"). This fluidic part was fabricated by structuring the Si wafer by deep reactive ion etching.
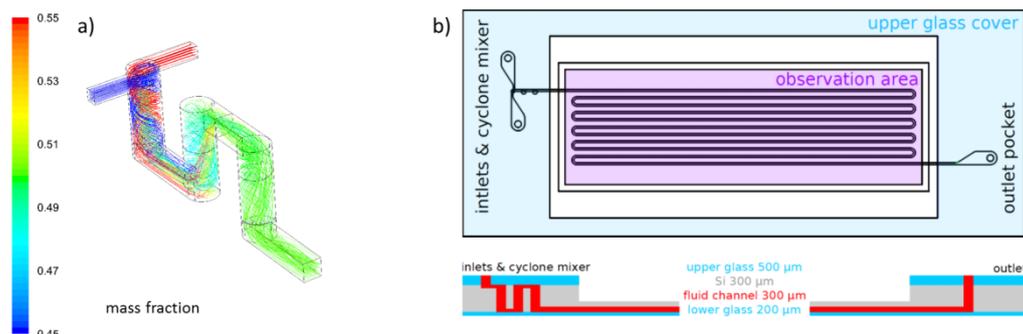
Figure 2. a) CFD simulation of the mass fractions passing through the triple cyclone mixer, resulting in a perfect mixing at the outlet. The color scale gives the mixing ratio, where 0.5 corresponds to a 1:1 mixture. b) Simplified construction drawing of the microfluidic chip with integrated triple cyclone mixer and observation lines (present meander design contains 3 straight sections).

The upper side of the chip was partially covered by 500 μm thick glass (blue shades, Fig. 2 b) and hosts inlet and outlet ports. In the central area of the chip the observation area is located, on the opposite side of the meander structure, which was especially thinned down by Si etching (conducted at IHM TUD) to allow experiments in transmission mode. Hence, the X-rays have to pass 300 μm of Si in addition to 200 μm of the lower glass layer and 300 μm of sample in the fluid channel. The bottom side of the chip is completely covered by a further 200 μm thick glass layer and acts as lid for the fluid channel (300 μm × 300 μm) in the meander. Holes in the top glass layer for the inlet and outlet ports and the cylinders for the cyclone mixer in the silicon chip were fabricated by laser drilling. Anodic bonding was used for the glass-Si parts and fusion bonding for the two 750 μm Si wafers. The present configuration is designed for a total flow of 2.5 kg h^{-1} (Reynolds number of 2300), a pressure drop of 12 bar, a dead time of 1 ms and an observation time up to 20 ms (time resolution < 1 μs along the channel due to high flow and small beam). To access longer reaction times, a capillary tube can be attached to the outlet, extending the observation time. Measurements can then also be conducted on the liquid as it is released from the capillary into a free liquid jet. An additional pressure drop of 2 bar for the fluidic rack is still within the operating conditions.

3. Results and Discussion

For experiments up to 20 ms observation time the silicon microreactor chip (schematic Figure 2 b) was used alone. The reaction of gold with THPC was investigated. After a certain equilibration time both in the chip and at the outlet (operating it as free liquid jet) oxidized gold was observed. An example spectrum at the outlet of the free liquid jet (residence time 20 ms) is shown in Figure 3 a.
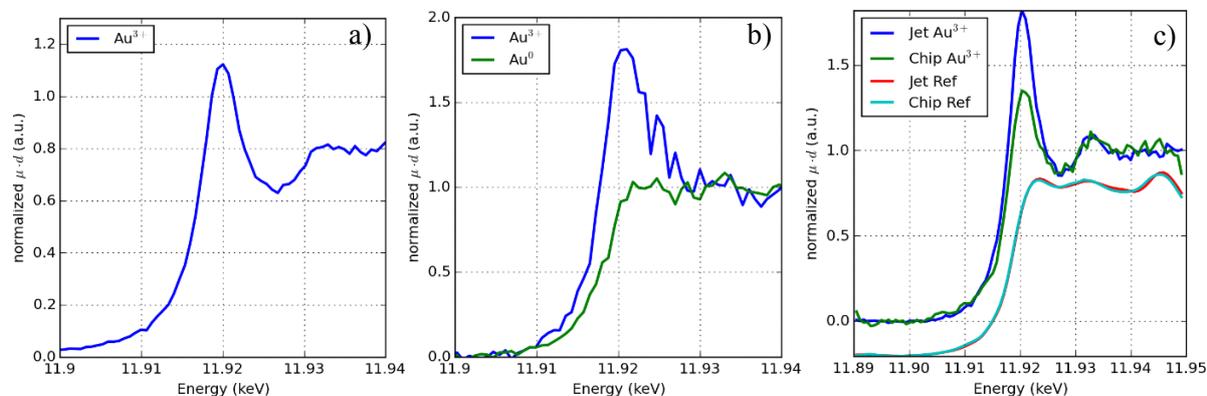
Figure 3. XANES spectra after (a) the Si-mixer (20 ms), (b) the capillary (3s, with (green) and without (blue) THPC), and (c) inside the microfluidic chip (Chip) and in the free liquid jet (Jet) for references of gold precursor solution (Au^{3+}) and metallic gold foil (Au^{0}).

In the chip itself fast deposition of metallic gold occurred at the position where the X-ray beam was hitting the Si chip despite of the high Reynolds number. Hence, $HAuCl_4$ was reduced by the X-ray beam, possibly enhanced by defect sites at the silicon wall (e.g. seeds for the reduced gold). As the residence time with 20 ms is rather short, we thus exploited the length of the reactor and additionally investigated the reduction using a longer capillary behind the microfluidic mixer. In this case, reduced gold was found (green spectrum in Fig. 3b, compared to reference samples in Fig. 3c). Hence, two different setups need to be used to detect the reduction kinetics in nanoparticle formation under the applied reaction conditions. In case the metal does not interact with the wall the X-ray kinetics of nanoparticle formation could be determined by scanning along the reactor. In case of gold reduction with THPC a free jet can be used, but under the present reaction conditions mostly Au^{3+} is found after 20 ms, however, Au^0 nanoparticles coud be found after 3 s. For gaining a full insight, more investigations are required using different precursor solutions and concentrations, different gold precursor/reduction agent ratios, defined equilibration time and different residence times in future.

4. Conclusion and Outlook

We have presented a microfluidic device, which allows investigation of reactions with millisecond resolution and does not depend on equally rapid acquisition of data as the spectra can be either taken along the microfluidic reactor or at its outlet (free liquid jet) for X-ray sensitive reactions as in the case of gold. A mixer (< 1 ms dead time) directly integrated on the chip was used to achieve rapid and thorough mixing. The fluidic rack is able to deliver the liquids with high volumetric flow rates as demanded by the experimental approach (turbulent mixing, rather homogeneous flow profile). Pressure driven fluid delivery worked very smooth and no pulsation or discontinuities were observed. This enables the investigation of very early reaction times (2 ms) as well as an external cyclone mixer for extended observation times (>20 ms). Measurements in the free liquid jet are promising, since no depositions can occur and little X-ray absorbing material is present. However, it is more tedious to resolve the temporal evolution of the reaction. This requires external delays (different channel length).

5. Acknowledgement

References

[1]   Grunwaldt J-D, Kiener C, Wögerbauer C and Baiker A 1999 *J.Catal.***181** 223-232
[2]   Wang F, Richards V N, Shields S B, and Buhro W E 2014 *Chem. Mater.* **26** 5–21
[3]   Thanh N T K, Maclean N and Mahiddine S 2014 *Chem. Rev.* **114** 7610–7630
[4]   Schubert K, Brandner J, Fichtner M, et al., 2001 *Microscale Thermophys.* Eng. **5** 17-39
[5]   Fräulin C, Rinke G, Dittmeyer R 2014 *Microfluid Nanofluidics* **16** 149-157
[6]   Kölbl A, Kraut M and Wenka A 2011 *Chem. Eng. J.* **167** 444– 454
[7]   Wagner J, Tshikhudo T and Kohler J 2008 *Chem. Eng. J.* **135** 104–109
[8]   Polte J, Tuaev X, Wuithschick M, Fischer A, Thuenemann A F, Rademann K, Kraehnert R and Emmerling F 2012 *ACS Nano* **6** 5791–5802
[9]   Abecassis B, Testard F, Kong Q Y, Francois B and Spalla O 2010 *Langmuir* **26** 13847–13854
[10]   Duff D G, Baiker A and Edwards P P 1993 *Langmuir* **9** 2301–2309
[11]   Biswas K, Varghese N and Rao C N R 2008 *Small* **4** 649–655
[12]   Hueso J L, Sebastian V, Mayoral A, et al. 2013 *RSC Adv.* **3** 10427
[13]   Hofmann G, 2015 Dissertation, Karlsruhe Institute of Technology (KIT), DOI(KIT): 10.5445/IR/1000049565.